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CERTAIN PRINCIPLES OF FORMATION OF POROUS CERAMIC STRUCTURES. PROPERTIES AND APPLICATIONS (A REVIEW)

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The current state of the production of porous ceramics is considered, mainly for high-temperature applications in various fields of engineering. A classification for these materials is proposed and the most commonly used methods for increasing porosity in ceramics are described.

Porous ceramics is usually understood as material with porosity over 30%. Practical implementation of the technology of porous ceramics in Russia and other countries started in 1930s. Although it may seen incredible, the principles of using such materials, including service at elevated temperatures, had not been formulated until that time, i.e., there had been no industrial production of heat-insulating refractories and other kinds of porous ceramics [1].

At present, various porous products are manufactured for the purpose of decreasing thermal conductivity, increasing gas and liquid permeability, and increasing the inner surface of pore space for impregnation.

Such materials are used in various fields of engineering [2]:

– heat insulation of buildings and thermal machines;

– heat insulation of aircraft, mainly spacecraft machinery;

– filtration of liquids, hot gases, melted metals and alloys;

– refining metals and alloys by inert gas blowing via porous ceramics;

– cooling hot surfaces by feeding pressurized gas via porous ceramics;

– catalyst carriers in various chemical processes, including high-temperature ones;

– electrolyte carriers in fuel elements;

– membranes for separation and purification of gas and liquids.

In principle, the contemporary state of ceramic technology makes it possible to produce porous ceramics from any nonmetal inorganic materials. Articles with porosity of 20 – 27% can be produced without great difficulties. However, production of porous ceramics with high and especially superhigh porosity requires special techniques.

There is no generally accepted classification of porous ceramics, since each sector of application (construction, metallurgy, etc.) has its own classification principles and norms. However, porous ceramic products can be classified according to the following characteristic attributes [3];

– chemical composition of initial material: silicate, aluminosilicate, oxide, oxygen-free, etc.

– porosity: moderate porosity (30 – 50%), high porosity (60 – 75%), and superhigh porosity (over 75%);

– physical state of products: piecewise, continuos, filling;

– inner structure: granular, cellular, fibrous;

– refractoriness correlated to service temperatures: low-melting (below 1350°C), high-melting (1350 – 1580°C), refractory (1580 – 1770°C), highly refractory (1170 – 2000°C), super refractory (over 2000°C);

– destination and application area: heat-insulating (main parameter: thermal conductivity); heat-shielding (main parameter: the product of heat conductivity and apparent density values), and permeable (main parameters: porosity, pore size, and permeability).

There are numerous methods for increasing porosity of ceramics. Their analysis and generalization suggest that theses methods are variants of the following main methods, which differ in principle:

– selection of a granular composition for initial molding mixture [4];

– introduction of natural or synthesized filler grains with their own porosity into the mixture [5];

– introduction of additives producing pores into an initial mixture and their subsequent removal by evaporation, sublimation, dissolution, or burning out);

– swelling of the whole mixture or its individual components in thermal treatment;

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– involvement of air into ceramics suspensions under mechanical treatment due to introduction of foam-forming additives or separately prepared foam;

– blowing gas into a melt or formation of gas and retaining gas bubbles;

– fixation of gas bubbles arising as a consequence of chemical reaction in ceramic suspension or decomposition of gas-forming additives introduced into the mixture [6].

– impregnation of a polymer cellular matrix with a ceramic suspension and subsequent squeezing out, drying, and thermal treatment to remove the organic components;

– introduction of ceramic fibers into a mixture and subsequent molding together with binders and thermal treatment of molded products [7];

– extrusion of plasticized ceramic mixtures using molding equipment that ensures immediate formation of a honeycomb structure.

Below we consider the specifics of these methods, the possibilities of using them for porous ceramics with various degrees of porosity and various structures, and application areas for these products.

Cavities arise in any packing of granular compositions. Porosity is facilitated by the grain shape being as close to a sphere as possible, by filler grains being monofractional, by a minimum possible content of finely disperse of liquid binder allowing for strength required in subsequent sintering; strength; by a minimum possible molding pressure allowing for required strength.

Compliance with the above conditions makes it possible to produce ceramics with porosity up to 40%, which has a uniform structure, pores of close sizes, and moderate strength and thermal resistance.

This method is used to produce porous ceramics containing grains of chamotte and various oxides, which are successfully used as filters, porous membranes for metal refining, dust purification of gases, catalyst carriers, fuel elements, and other purposes.

A perceptible increase in porosity is achieved by introducing granules with their own high porosity: natural granules (diatomite, tripolite, swelled perlite and vermiculite) and granules produced by crushing of briquettes prepared by foaming or another method. Porosity can be increased by increasing the inner porosity of granules or increasing their size to a reasonable limit, as well as by the same factors that were listed for the preceding method.

Recently new methods have been developed for producing hollow spheres from various materials, including highly refractory ones (Al_2O_3, ZrO_2, etc.), which makes it possible to eliminate crushing and screening operation and obtain a filler with sphere-shaped grains and large cavities, however, the cost of such spheres is as yet very high [8].

The introduction of porous granules can additionally increase porosity by 10 – 15%. Application of such ceramics is similar to articles with compact filler grains, besides, ceramics with hollow spheres can act as effective thermal insulation.

A rational accessible and relatively cheep method is introduction of additives subsequently removed. Of all specified variants of this method, the one extensively used is the method of introducing burning-out additives, which can be represented by any combustible material that is economically justifiable. These materials include wood and wood-processing products (sawdust, lignin), various types of coals and coking products, cereal grain husk, etc.

Ceramic component of mixtures can be fine- or coarse-grained. They are mixed with burning-out additives, then intermediate articles are molded by compression, plastic molding, or slip casting. The most suitable for refractory articles are low-ash additives such as petroleum or pitch coke, as well as swelling polymer granules, in particular polystyrene with high proper porosity.

The porosity of articles with burning-out additives depends on their type, content, and the grain size. A maximum content of such additives is limited by the fact of loosening and abrupt decrease in strength of material. Such ceramics should be fired in an oxidizing medium until complete burning-out of the additive.

The method of introducing burn-out additives makes it possible to produce ceramics with porosity up to 60 – 65% and introducing polystyrene, up to 80 – 85%. These products due to their special structure have low thermal conductivity and are suitable as efficient thermal insulation [9].

The method of a mixture swelling under heating is based on the ability of certain natural materials to abruptly increase their volume due to the formation and expansion of gas at a moment when the material is in the pyroplastic state. Thus, intense swelling is found in some clays, which is the basis for claydite production, and also in vermiculite, perlite, and some minerals of the quartz group.

Involving air into a suspension when making porous ceramics (foam ceramics) is widely used to produce articles with extremely high porosity. Uniform finely cellular foam can be produced by such frothing agents as colophony soap, saponin-alginate, aluminosulfonaphthylene, etc. When mixed with a suspension, the stability of emerging three-phase foam increases. Such cellular structure is preserved under subsequent drying and firing.

The structure and porosity of foam ceramics depend on the density of the solid ceramic phase, the moisture, viscosity, and pH of the suspension, the content of foam introduced, and the type of the foaming additive. This method is used to produce articles from various materials with porosity of 80 – 85% (chamotte, dynas, oxide, silicon carbide, silicon nitride, etc.) that have relatively high strength, low thermal conductivity, and low density, which allows for their wide application as thermal insulation and thermal protection.

The method of gas blown in or gas formation in a melt did not acquire practical application with respect to porous ceramics due to high viscosity of the melt and the complexity, high cost, and low technological suitability of the method, however it is widely used in glass industry for producing foam glass.

The method of chemical formation of pores in suspensions is sufficiently widespread in production of highly porous articles. Gas-forming additives used should ensure formation of a large volume of gases, a uniform release of gas within a prescribed temperature interval, and should not be toxic.

Among numerous chemical reactions involving gas formation, the ones practically used are reactions between carbonates and acids, between some metals (for instance, aluminum) and acids, and also reactions of decompositions of carbonates, peroxides, etc. The reaction between aluminum powder and orthophosphoric acid can produce non-fired porous ceramics curing at a temperature around 300°C due to the formation of phosphates with binding properties.

The process of formation of a cellular mixture in chemical formation of pores depends on many factors: the suspension viscosity, the temperature, type, content, and dispersion of solid gas-forming agent, the type of acid and its content, the presence and content of a stabilizer for swelled mixture. This method provides for production of ceramics with high and superhigh porosity based on various initial materials, which is used in thermal insulation and heat-shielding.

Porous ceramics can be obtained by a ceramic suspension impregnating an elastic matrix with cells of different sizes made of a polymer materials, for instance, foam-polyurethane. The latter is vacuum-treated, saturated with suspension, then a part of suspension is removed by pressing between rolls. An intermediate product is dried and fired to burn out the organic matrix (polymer). The resulting porous ceramics repeating the configuration of the polymer sponge has very high permeability and filtering capacity. It is used for purification of ferrous and nonferrous metals by melt filtration.

A very efficient method for producing cellular ceramics is extruding plasticized mixtures through a die of a preset configuration. The method is difficult to implement with a non-plastic ceramic material. This called for finding suitable plasticizing and binding agents to impart plasticity to mixtures and the development of special nozzles and dies for extruding mixtures. As a result, a structure of multifaceted cells interconnecting through openings in facets was obtained. Such articles are now widely used as filters, catalyst carriers, membranes for purification and separation of fluids (oils, medicines, wine, etc.).

The method of producing and using fibers has been known for a long time. However, the maximum service temperature, for instance, of fiberglass does not exceed 600°C. After industrial implementation of kaolin fiber technology and, recently, the development of techniques for obtaining fiber materials from highly refractory oxides (Al_2O_3, ZrO_2, etc.) it has become possible to dramatically raise the temperature of service of porous fiber ceramics and to expand its application areas.

Fibers are used to make fabrics, mats, pipe, plates, large heat-insulating blocks. Of all known inorganic binders (bentonite, sodium silicate glass, silica gel, aluminophosphates and chromophosphates) the latter are the most suitable. A search for even more efficient binders for extremely high temperatures is in progress.

Articles made of fibrous materials in the form of large modules with very low thermal conductivity make its possible to lighten furnace installation, save fuel, and shorten the firing cycle [10].

The properties of porous ceramics depend on the type of initial material, porosity and structure of articles. Characteristics of the structure include total, open, and sealed porosity, permeability, pore size and pore distribution by sizes, and specific surface area. The most significant structural parameters are porosity and pore size. The latter can vary over a wide range from a fraction of a nanometer to a few millimeters.

The role of structure in porous ceramics for different destinations is not identical. An active pore space in permeable filtering products is created only by intercommunicating channel-shaped pores. In catalyst carriers, isolated open pores as well can have an active role. In heat-insulating products, all pores act as barriers to heat propagation.

Porous ceramics has several main types of structure, which mostly depend on the pore-formation method.

Pourous ceramics with a granular structure has a skeleton filled by filler grains cemented by a binder. Its has pores of irregular shape and no open pores. The gaseous phase in most cases is a continuous phase, whereas the solid phase is nearly totally discontinuous.

Porous ceramics of this type has substantial strength, moderate thermal conductivity and gas permeability, and good thermal resistance. An introduction of burning-out additives, which increase porosity, perceptible decreases the strength and thermal conductivity and increases permeability.

Cellular ceramics with a sintered skeleton (for instance, Al_2O_3, ZrO_2, BeO, etc.). contains dense sintered bridges and spheroid cavities. The degree of continuity of the skeleton, the ratio of sealed air cells to intercommunicating ones depend on the porosity of articles. Ceramics of this type usually has high porosity, increased strength, including when loaded under heating, and thermal conductivity, low thermal resistance, low gas permeability under a continuous skeleton, which perceptibly grows when the skeleton continuity is disturbed.

Cellular ceramics not having a sintered skeleton (for instance, SiC, Si_3N_4, melted quartz) has partly sintered porous bridges and spheroid cavities. Such ceramics can have very high porosity, since fire shrinkage in these poorly sinterable materials is insignificant or absent. Such ceramics typically has relatively low strength, moderate permeability, which is not typical of cellular ceramics, decreased thermal conductivity due to porosity of bridges, and high thermal resistance (the latter is probably due to the nature of such materials as SiC, Si_3N_4, and SiO_2).

In cellular structure types with substantial continuity of the skeleton, the solid phase is predominantly continuous and

TABLE 1

Initial material	Total porosity, %	Production method	Thermal conductivity, W/(m · K) at temperature	
			500°C	1000°C
Al_2O_3	70	Foaming	1.86	1.34
		Introduction of burning-out additives	0.61	0.51
ZrO_2	60	Foaming	0.53	0.65
		Introduction of burning-out additives	0.16	0.28

TABLE 2

Initial material	Thermal conductivity, W/(m · K), at mean temperature of 800°C	TCLE in temperature interval 20 – 1000°C, 10^{-6} K^{-1}	Thermal resistance, number of thermal water cycles (850 – 20°C)
SiO_2**	0.24	0.5	20
SiC	0.73	4.5	10
BeO	2.67	9.3	6
Al_2O_3	0.87	8.5	2
ZrO_2***	0.19	10.7	1

* In all cases total porosity is 82 – 93%.

** Melted quartz.

*** Stabilized ZrO_2.

the gaseous phase is partly disrupted. A cellular structure allows for the production of articles with a maximum (up to 90%) porosity. Combined types of structures are possible as well, for instance, when cellular foam-ceramic or foam-polystyrene is introduced into a mixture of granules.

Porous ceramics with the fibrous structure has an elastic-rigid skeleton formed by thin interwinding filaments with point contacts with the binder. Pores in this type of ceramics are open and interconnecting. Increased porosity is usually achieved by elongated fibers.

There are three variants of a fibrous structure: random (disordered) arrangement of fibers in the volume of an article, an ordered arrangement, and a combined arrangement. The degree of nonuniformity is characterized by the anisotropy coefficient. This type of ceramics has a high extent of cavities, high permeability, low thermal conductivity, and low strength.

Some properties of porous ceramics, which can be determined by destroying an articles (for instance, true density and refractoriness), as well as the TCLE do not depend on porosity and are determined only by the nature of initial material. All other properties depend on porosity and structure. This is true of permeability, strength under normal or elevated temperatures, creep, elasticity modulus, thermal conductivity, thermal resistance, evaporability at high temperatures, and volume constancy (additional shrinkage) in heating.

In the case of equal porosity, a deciding factor is the structure of the product, which can be demonstrated with thermal conductivity (Table 1), and with equal porosity and similar structures, many properties, such as thermal conductivity, TCLE, and heat resistance depend on the type and properties of the solid phase (Table 2).

The properties of non-refractory porous ceramics are scarcely described in the literature. For instance, articles made of foam-diatomite, diatomite with burning-out additives, and ceramic perlite are usually specified by apparent density, which is, respectively, 0.35 – 0.45, 0.50 – 0.70, and 0.25 – 0.40 g/cm^3. Compressive strength in articles with such density does not exceed 0.6 – 1.0 MPa. These articles have very low thermal conductivity: within a range of 0.15 – 0.22 W/(m · K) at a temperature of 350°C and can serve at a temperature below 1000°C.

A unique combination of various properties provides for extensive use of porous ceramics in various sectors of contemporary technologies, from construction to space engineering.

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